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Donald W. Johnson

POLAROGRAPHIC ANALYSIS APPLIED TO METALLURGICAL SOLUTIONS AND PRODUCTS

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A Thesis
Submitted in Partial Fulfilment of the
Requirements for a Degree of Bachelor
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The polarograph has been applied to a large number of chemical and metallurgical analyses, and is especially applicable to solution control analysis and to the determination of minute quantities of ions in the presence of large amounts of other ions. Practically any substance that undergoes oxidation or reduction can be analyzed successfully polarographically, and processes have been developed for the estimation of organic compounds and even some colloids. The purpose of this thesis is to test the applicability of polarographic methods to zinc leach solution control analysis, and to test their use in the analysis of minor constituents or alloying elements in various metallurgical products.

In addition to the zinc leach solution, successful analyses were made on samples of Anaconda zinc purification cake, on copper solutions after electrolytic stripping, on cadmium-zinc distillation products and residues, and on the copper content of copper-iron alloys. With the exception of the copper-iron alloys, copper, cadmium, and zinc were determined from one solution. Polarographic

methods resulted in much more rapid determinations than do standard "wet" processes because of the few preliminary preparations, other than dissolving the sample and dilution, and because several ions can be analyzed without having to be separated.

INTRODUCTION

Since the polarograph is a relatively new analytical instrument, a short discussion of polarographic history, theory, and calculations may be useful before the description of specific analytical applications.

HISTORY:

Professor Jaroslav Heyrovsky, of the Charles University, Prague, Czechoslovakia, in 1925 conceived the idea that both qualitative and quantitative analysis might be made by interpreting the height and position of the waves in a current-voltage curve, plotted when an electromotive force is impressed upon an ionized solution.[1] During the same year Heyrovsky and Shikata constructed the first polarograph and employed a dropping mercury-mercury pool electrode system which had been used for other purposes

1. Kolthoff, I. M., and Lingane, J. J., Polarography, Interscience Publishers, New York, 1946, p. 3.

earlier. Immediately the polarograph became the subject of much study in Europe, but the first monograph on polarography written in the United States did not appear until 1941.[1] Since then, so many publications on the subject have been issued that only a few scientific instrument manufacturers maintain up-to-date bibliographies.

Beside its wide application to inorganic analysis, the polarograph is widely used to analyze organic substances, to determine traces of metals, such as arsenic or lead, in the human body, and to study oxidation-reduction tendencies and rates.

THEORY:

The polarograph is a self-contained unit consisting essentially of a method of impressing an adjustable, controlled electromotive force upon an ionized solution, and of measuring the magnitude of the resulting current. The electrodes are mercury; one is a calm pool having a relatively large area to minimize polarization, and the other is a very small drop formed by a capillary tube. The purpose of the continually-forming drop is to promote polarization and, at the same time, to provide a fresh surface at all times.

1. Lingane, J. J., "Polarographic Theory, Instrumentation, and Methodology", Analytical Chemistry, Vol. 21, No. 1, January 1949, pp. 45-60.

The basis of polarography is the formation of a very thin envelope of solution, immediately surrounding the dropping mercury electrode, in which ions are discharged as rapidly as they migrate to it. When they are discharged, the ions may enter into an amalgam with the mercury, adhere to the surface of the mercury as a scum, or lose only part of their valence electrons and return to the solution in a lower valence state.[1] When the last occurs, two polarographic waves will result from the same ion, as in the case of copper or cobalt. The migration of the ions into the polarized film of solution around the drop is caused by an electrical force produced by the potential difference between the drop surface and the solution, and by a diffusive force produced by the concentration gradient between the polarized envelope around the drop and the body of the solution.[2]

The electrical force must be eliminated, or at least minimized, because it is not proportional to the ionic concentration. Since the current through the solution is carried by all the ions in the solution, regardless of whether or not they undergo any electrode reaction, the electrical force can be reduced to a negligible effect by

1. Hohn, H., "Mercury in Chemical Metallurgy", Research 3-1, (Microfilm Copy)
2. Kolthoff, I. M., and Lingane, J. J., Polarography, p. 15.

the addition of a relatively high concentration of supporting electrolyte. The supporting electrolyte is usually a salt whose ions do not undergo any electrode reaction in the voltage range of the half-wave potentials of the ions under investigation. Then the only effective force causing the ions to enter the polarized envelope is that of diffusion; the current is directly proportional to the rate of diffusion, which in turn, is directly proportional to the concentration gradient between the polarized envelope and the theoretically inexhaustible supply of ions in the body of the polarographic solution.[1]

Qualitative analysis is made possible by the half-wave potential, the position of which is constant and reproducable for any particular ionic gain or loss of electrons. The half-wave potential varies slightly with the concentration of the ion under investigation, but it can be changed considerably by changing the supporting electrolyte, by changing the valence state of the ion, or by combining the ion into ammonio, aquo, cyano, or other complex ions. In the same electrolyte, cobalt produces half-wave potentials of -0.3 and -1.3 volts in the trivalent and bivalent states respectively; cupric ions in 1 N NH_4OH and 1 N NH_4Cl produce a half-wave potential of -0.24 volts and cuprous ions pro-

1. Kolthoff, I. M., and Lingane, J. J., Polarography, pp. 17-18.

duce one at -0.50 volts, whereas, in 0.1 N KCl electrolyte, the half-wave potential of copper falls at +0.02 volts.[1]

The foremost source of trouble in polarographic analysis is the formation of maxima in the current-voltage curves. The maxima are pronounced peaks occurring at the top of the wave, and are so erratic that they cannot be evaluated relative to the ion concentration. They are called positive and negative dependent upon the side of the electrocapillary zero point on which they appear. The electrocapillary point is that voltage at which the potential of the mercury drop is zero with respect to that of the mercury pool. Although a negative potential is impressed across the solution, the drop is positive with respect to the normal calomel electrode until the applied voltage has been increased to -0.56 volts. The positive potential is induced by the mercury passing through the capillary tube, the change in the surface tension of the growing drop, and other associated physical forces. The electrocapillary zero point may be changed, and maxima suppressed by capillary-active ions, ions which react with the mercury drop. Capillary-inactive ions are also effective in suppressing maxima: anions are most effective against positive maxima, and cations against negative maxima.[2] Various organic dyes in the solution are

1. Kolthoff, I. M., and Lingane, J. J., Polarography, p. 482.
2. Ibid., p. 117.

effective in suppressing various specific maxima, but probably the most generally effective suppressor, and the simplest to use, is gelatin. Most metallic maxima can be effectively suppressed by adding sufficient gelatin to bring its concentration to 0.001%, but high concentrations of gelatin tend to suppress the limiting current.[1]

Oxygen is the most prevalent and erratic maximum producer, but its maximum can be suppressed by passing nitrogen, or some other inert gas, through the solution for about five minutes prior to the analysis, and by maintaining an inert gas atmosphere above the solution during the analysis. The oxygen maximum can also be eliminated by the addition of sodium sulfite to neutral or alkaline polarographic solutions, unless one or more of the desired ions will be precipitated as the sulfate.

Some maxima appear only at higher concentrations, and can be eliminated only partly by gelatin or other suppressors. Often complete suppression can be accomplished by further dilution of the polarographic solution.

POLAROGRAPHIC CALCULATIONS:

The basis for the interpretation of the height of current-voltage waves is the "Ilkovic Equation."[2] By re-

1. Kolthoff, I. M., and Lingane, J. J., Polarography, pp. 121-124.
2. Ibid., p. 55.

lating the drop time and the rate of mercury flow to the magnitude of the diffusion constant, such variables as capillary diameter, pressure on the mercury, and temperature are taken into consideration. Ilkovic's Equation is expressed:

$$i_d = 605nD^{\frac{1}{2}}Cm^{2/3}t^{1/6}$$

where:

i_d is the average current during the drop period, and is the product of the milliampere reading and the sensitivity,

n is the number of electrons affected by the reduction or oxidation of the ion producing the wave,

D is the diffusion constant of the ion expressed in cm^2/sec,

C is the concentration of the ion producing the wave, in terms of millimoles per liter,

m is the rate of mercury flow in milligrams per second, and

t represents the time of formation of the mercury drop, in seconds.

The Ilkovic Equation has been proved experimentally, but the large number of variables in practice make its application difficult. If, however, all these variables can be accurately evaluated, the concentration of the wave-producing ion can be calculated directly from the equation.

In order to get away from the evaluation of these variables, several comparative or indirect calculation procedures have been developed. The two most used are the methods in which pilot ions and in which graphs plotting wave height versus concentration are used. The latter procedure requires at least three polarographic solutions: the unknown, and two standard solutions of different concentrations, all three in the same supporting electrolyte. The two standard solutions are polarographed, and a linear graph is established relating the height of the wave produced by each concentration. Then the unknown solution is analyzed, its wave height plotted on the graph, and the concentration read from the graph.

Only one polarographic solution is required in the pilot ion method. After the unknown sample has been recorded on the polarogram, a very small volume of a solution containing a predetermined concentration of the ion in question is added to the polarographic solution, and a new polarogram is recorded. Then the concentration of the desired ion can be calculated from the relative heights of the waves of the unknown ion and of the unknown plus the added amount of the same ion. The pilot ion is also useful in identifying strange waves. If the ion responsible for a certain wave is uncertain, a few drops of the suspected

ion may be added and a rise in the wave indicates the presence of that ion. This procedure is not generally recommended because of the near proximity of the half-wave potentials in many cases; cobalt produces two waves, the first falling in the second copper wave and the second coinciding with the zinc wave.

Lingane and Loveridge[1] proposed a method of analytical calculation involving a diffusion current constant,

$$I = \frac{i_d}{Cm^{2/3}t^{1/6}}$$

whereby all variables are included in one symbol. Rearranging Ilkovic's Equation, and substituting I produces

$$I = 605nD^{\frac{1}{2}}.$$

Here n and D are constant for solutions containing comparable amounts of the same ion in similar valence states, and in identical supporting electrolyte concentrations.[2] Thus if a preliminary analysis is made on the unknown, a rough estimate of the ionic concentrations can be made, and a standard solution can be made up to contain about the same concentrations.

1. Lingane, J. J., and Loveridge, Brian A., "Fundamental Studies With the Dropping Mercury Electrode. IV. Empirical Modification of the Ilkovic Equation", Journal of the American Chemical Society, Vol. 68 (1946), pp. 395-397.
2. Taylor, John Keenan, "Examination of Absolute and Comparative Methods of Polarographic Analysis", Analytical Chemistry, Vol. 19, No. 6, June, 1947, pp. 368-372.

Then when the unknown and standard solutions are analyzed consecutively, and their polarograms recorded,

$$I_{standard} = I_{unknown}$$

and

$$\left(\frac{i_d}{Cm^{2/3}t^{1/6}}\right)_{standard} = \left(\frac{i_d}{Cm^{2/3}t^{1/6}}\right)_{unknown}$$

By cancelling similar quantities and rearranging:

$$C_{unknown} = \frac{i_{d\ unknown}\ C_{standard}}{i_{d\ standard}}$$

Here the concentration is not limited to terms of millimoles per liter, but can be expressed in any terms in which the prepared standard is measured. This method was employed for all calculations involved in this thesis. The advantages of this procedure are:

1. Only one initial polarogram need be made to determine the ions present; on subsequent analyses none are required,
2. Results may be calculated in any desired terms with no conversion, and
3. Variables, such as drop time, rate of flow of mercury, temperature, and galvanometer variations are minimized by analyzing the standard and the unknown consecutively.[1]

1. Ibid., p. 372.

POLAROGRAPHIC CONTROL ANALYSIS OF ZINC LEACH SOLUTION

In the analysis of a solution by "wet" analytical methods, a large volume of solution is generally required, and the preparation of that solution for the analysis is time-consuming. The analysis of zinc leach solution is the basis upon which is determined the amount of zinc dust that must be added to the solution to precipitate the cadmium and copper. Beside the large volume of solution required, "wet" methods of analysis take a long time and produce results of a degree of accuracy not required for this type of work. The polarograph is accurate to plus or minus 2%; this degree of error would not be serious in routine control analysis. If a set of standards were made up and the calculations tabulated so that the galvanometer deflection could be inserted into a table to show the percentage compositions, any employee who has been shown the operating procedure could produce accurate analytical results.

In order to produce the waves of copper, a supporting electrolyte composed of 1 N NH_4OH and 1 N NH_4Cl, with a small amount of gelatin was used. One milliliter of the leach solution is added to 2.6749 grams of solid NH_4Cl in 6.36 milliliters of concentrated NH_4OH. 0.0072 grams of gelatin are added, and the solution diluted with water to

a volume of fifty milliliters. A standard comparison solution is made up to contain a concentration of 0.1 gram per liter of cadmium, copper, and zinc in the same electrolyte solution.

After passing nitrogen gas through the solutions for five minutes, the nitrogen tube is raised to maintain an inert gas atmosphere above the surface of the solution. This procedure expels oxygen from the solutions and prevents its reentrance. Both solutions are analyzed and their polarograms recorded on the same graph paper or film. From the relative heights of the waves produced by the various ions in solution, the ionic concentrations can be calculated.

In an effort to convert the sulfates in the leach solution to chlorides, the sulfate radical was precipitated with barium chloride. The copper, cadmium, and zinc assays were all lower than the results obtained when the sulfate ion was allowed to remain. When a supporting electrolyte composed of 1 N $(NH_4)_2SO_4$ and 1 N NH_4OH was employed, the results of several analyses of the same solution were inconsistent.

Some of the sulfate radical of the sulfuric acid in the sample was converted to ammonium sulfate when the sample was ammoniated, but the NH_4Cl was the actual electrolyte, and was buffered by the NH_4OH. No other methods of analysis were used in this case as a check, but the results of several analyses of various concentrations against various

standards agree quite closely. The entire analysis, from the receipt of the sample through the calculation of the results, could be carried out in one-half hour. The concentrations, in terms of grams per liter, were: cadmium, 10.82; copper, 0.147; and zinc, 102.75.

ANALYSIS OF ZINC PURIFICATION CAKE

A sample of Anaconda zinc purification cake was effectively analyzed polarographically for the copper, cadmium, and zinc contents. The analysis was much more rapid than a "wet" analysis because the various metal ions did not have to be separated prior to their determination. Well-defined waves were obtained from each of the elements, and nitrogen and gelatin suppressed the oxygen and zinc maxima. The same standard solution used for the zinc leach solution was used in this analysis.

The sample of zinc purification cake weighing 0.5000 gram was dissolved in concentrated hydrochloric and nitric acids. After evaporating to dryness, the residue was picked up in a measured volume of water, in this case, 100 milliliters. The polarographic solution was made up of five milliliters of the sample solution, 2.6749 grams of solid NH_4Cl, 6.36 ml. of concentrated NH_4OH, and 0.0072 grams of gelatin; the solution was diluted to a volume of fifty milliliters with water. The standard and the sample were saturated with nitrogen and their polarograms were recorded. A span E. M. F. of one and one-half or two volts is necessary since the half-wave potential of zinc is -1.28 volts.

From the relative heights of the waves produced by each of the similar ions, their concentration in the sample solution can be calculated, and from that, the percentage

composition of the solid sample. In these calculations, all solution volumes must be accurately measured because the volumes are the basis for the accuracy of the results. The formula used is:

$$\% \text{ Comp.} = \frac{C_{st}\ H_u\ S_u\ V_u\ V_a\ x100}{H_{st}\ S_{st}\ V_b\ W}$$

where C_{st} is the concentration of the standard solution in grams per ml., H_u is the height of the wave produced by the ions in the unknown solution at the sensitivity S_u, H_{st} and S_{st} are the height and sensitivity of the standard solution wave, V_u is the volume of the unknown polarographic solution, V_b is the amount of the total sample solution, V_a, added to the polarographic solution when it was made up, and W is the sample weight.

The saving in time by analyzing polarographically may be important if a large number of similar samples are to be run, but the accuracy is not as high as that produced by standard wet analytical methods. A comparison of results of Bureau of Mines assays and polarographic analysis shows:

	Bureau of Mines	Polarographic
Cadmium	1.6%	1.662%
Copper	10.56%	10.23%
Zinc	41.8%	40.95%

POLAROGRAPHIC ANALYSIS OF COPPER IN IRON

The polarograph is valuable for analyzing many impurities or minor alloying elements in metals. This is especially true if the half-wave potential of the impurity occurs at a lower negative value than does that of the base metal, and the two do not have to be separated. In the case of copper in iron, the copper waves are most successfully produced in a supporting electrolyte of ammonium hydroxide and chloride. In this mixture, the iron is precipitated, and, being in such large concentration, it must be filtered out to prevent covering the mercury pool completely.

The sample to be analyzed was dissolved in concentrated nitric and hydrochloric acids, and the solution evaporated to dryness to prevent the formation of excess ammonium chloride when the solution was ammoniated to precipitate the iron. After the $Fe(OH)_3$ was removed, the solution was again evaporated to dryness, and a rough estimate of the ammonium chloride content was made. Enough NH_4Cl was added to bring its concentration to 1 normal, 6.36 ml. of NH_4OH and 0.0072 grams of gelatin were added, and the solution was diluted to fifty milliliters.

A copper standard solution and the unknown were run and the copper content of the sample was calculated using

the same formula as was used in the analysis of zinc purification cake. A sample of iron containing copper was analyzed giving a copper percentage of 1.313%. Later a larger sample of the same metal was analyzed against a different standard, and the copper value was found to be 1.310%. This particular set of analyses was in the closest agreement of results of a series of such sets.

Since aluminum is also precipitated by NH_4OH, the same procedure should be applicable to the analysis of copper in aluminum. In the case of either iron or aluminum, the initial sample weight, and the volume of the initial sample solution added to the polarographic solution should be determined by the suspected copper content of the alloy.

ANALYSIS OF NEUTRAL DORR OVERFLOW SOLUTION

A volume of Anaconda neutral Dorr overflow solution was procured for an experiment on zinc dust purification, and was analyzed in connection with that experiment. The solution was subjected to polarographic analysis, and the results were in good agreement, although the copper and cadmium results were lower than those produced by the "wet" analyses.

One milliliter of the solution was added to a fifty ml. polarographic solution and the waves produced were compared to those produced by a standard solution. The supporting electrolyte was 1 N NH_4OH and 1 N NH_4Cl with gelatin as a zinc maxima suppressor. The polarographic determination took approximately twenty minutes to perform and required a solution volume of only one milliliter. A "wet" analysis would have required a much larger volume of solution with a longer time spent concentrating the cadmium and copper.

A comparison of the results showed

Cadmium	0.39 and 0.333 grams/liter,
Copper	0.66 and 0.497 grams/liter, and
Zinc	109.7 and 106.8 grams/liter

for the "wet" and the polarographic methods respectively. This degree of accuracy should be sufficiently high for most solution control work.

CONCLUSION

Several specific procedures have been described both for solid and for solution analysis, as they were carried out in the laboratory. Where other analytical methods have been applied to the same samples, the results of polarographic analysis have been in good agreement. For solution analysis, the polarograph is excellent because of the small volume of solution required. In most cases, one milliliter of the solution to be analyzed is sufficient. A leach solution made up in the laboratory contained so high a concentration of zinc that only about one-tenth milliliter was used in the zinc analysis. The rapidity of the sample preparation is another asset in the use of the polarograph. If a number of samples are to be analyzed for the same elements, galvanometer readings need only be taken before and after each wave, but this procedure will produce a greater degree of error in that no consideration is taken of the gradually rising residual current.

Care should be taken in preparing samples and standards to have the ions in the same state of oxidation, and to have the supporting electrolytes the same concentration. Further study should be made on the depressing effect of gelatin on various metallic maxima. If gelatin is added in excess of that required to suppress maxima, it will also suppress

the limiting current.[1] At a concentration of 0.1 g/l of zinc, the maximum was not completely suppressed by 0.01036% gelatin, but was by 0.01446%. Occasionally maxima of metals, such as Indium, cannot be completely suppressed with gelatin. This usually occurs at fairly high concentrations, and the maximum can often be eliminated by dilution of the polarographic sample.

Since the accuracy of the polarograph is about a plus or minus 2%, it is much more adapted to dilute solutions or to impurities in the presence of large concentrations of other ions. Procedures have been described in the literature for polarographic analysis of such small concentrations as that of sulfur in gasoline and that of arsenic in pulped samples of human organs in suspected poison cases. The practicable applications of the polarograph in the field of metallurgy are practically limitless because of the small sample weight required, because of the rapidity of the analysis, and because of the little sample preparation required.

1. Kolthoff, I. M., and Lingane, J. J., Polarography, pp.122-124.

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